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Specification and Drawings, as originally filed, with Application for Patent Serial  
No: 2,423,712, on March 26, 2003, by **LE GROUPE LYSAC INC**, assignee of David  
Bergeron, Nicolas Nourry and Claude Couture, for "Crosslinked Amylopectin by Reactive  
Extrusion and Its Use as an Absorbent or Superabsorbent Material".

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**ABSTRACT**

The present invention relates to crosslinked amylopectin as well as to the preparation of a crosslinked amylopectin based absorbent or superabsorbent. The crosslinked amylopectin is prepared by reactive extrusion.

**TITLE OF THE INVENTION**

**CROSSLINKED AMYLOPECTIN BY REACTIVE  
EXTRUSION AND ITS USE AS AN ABSORBENT OR SUPERABSORBENT  
MATERIAL**

**5 FIELD OF THE INVENTION**

The present invention relates to crosslinked amylopectin prepared by reactive extrusion and its use as an absorbent or superabsorbent material.

**BACKGROUND OF THE INVENTION**

10 Superabsorbent polymers are primarily used as absorbents for biological fluids, water and aqueous solutions, primarily in diapers, adult incontinence products, as well as in feminine hygiene applications. Polyacrylates, polyacrylamides and their copolymers are among the best known superabsorbents. Alternative acrylic superabsorbent polymer forms, including  
15 partially biodegradable materials, are described in "Modern Superabsorbent Polymer Technology", (Buchholz F. L. and Graham A. T. Eds., Wiley-VCH, New York, 1998).

Polyacrylates constitute a major portion of the commercially available superabsorbents. However, their biodegradability is  
20 questionable, especially for the high molecular weight polymers. These polymers, composed of monomers such as acrylic acids and acrylamides, upon decomposition lead to the formation of residual monomers showing toxicity and allergenicity. Furthermore, these kinds of synthetic polymers have also been grafted onto polysaccharides.

25 Superabsorbent polysaccharide-based grafted-polymers are obtained via the grafting of an unsaturated monomer (acrylonitrile, acrylic acid, acrylamide) onto starch or, less frequently, cellulose. The so-obtained

polymers, also called "Super Sturper", have shown a water absorption ranging from 700 to 5 300 g/g in deionised water and up to 140 g/g in a 0.9 % saline solution (Riccardo P.O., Water-Absorbent Polymers: A Patent Survey. J. Macromol.Sci., Rev. Macromol. Chem. Phys., 1994, 607-662 (p.634) and cited references). Despite their very high water absorption capability, the grafted polysaccharides prepared by radical polymerization are not known to be biodegradable and hypoallergenic.

Polyaspartates have also been shown to offer good absorbing properties (Ross et al. US 5612384). However, polyaspartates appear to possess several drawbacks regarding their low molecular weight. Moreover, polyaspartates are synthetically made which constitutes an additional drawback (Koskan et al. 5221733). Furthermore, these polymers are strongly ionic and are thus subject to performance fluctuations in saline solutions.

Carboxymethylcelluloses (CMC) (Modern Superabsorbent Polymer Technology, Buchholz F. L. and Graham A. T. ed., Wiley-VCH, Toronto, 1998, pages-239-241 and cited references), and carboxymethylstarch (CMS) (Gross and Greuel, US 5,079,354, Jan. 7, 1992,) constitute other known polysaccharide-based superabsorbents. Cost has always been an issue with these superabsorbents, and they can therefore not be used alone in order to compete with the synthetic polymers. Moreover, these polymers are strongly ionic, as is the case for polyacrylates and polyaspartates, rendering them subject to performance fluctuations in saline solutions. Nonetheless, these products can be used in synergistic formulations, leading to cost effective superabsorbent materials (Bergeron, CA 2,382,419, filling date: April 24, 2002).

Natural polysaccharide-based superabsorbents constitute a very attractive class of polymers, considering that they can be biodegradable and hypoallergenic, in addition to the fact that they are made from renewable sources such as starch. Polysaccharides have been previously used in an extrusion process for the preparation of non-crosslinked starch-based materials as absorbents for liquids (Huppé et al. CA 2,308,537). A maximum Free Swell

Capacity (FSC) of 7.5 g/g in a 0.9% saline solution was obtained.

The use of extruders as continuous reactors for processes such as polymerization, polymer modification or compatibilization of polymer blends, involves technologies that are gaining in popularity and that are competing with conventional operations with respect to environmental considerations, efficiency and economic operators. In the case of reactive extrusion several organic reactions can be conducted in extruders, including polymerization, grafting, copolymer formation, crosslinking, functionalization and controlled degradation (Reactive Extrusion: Principles and Practice, Xanthos M. Ed., Hanser Publishers, New York, 1992). This technology has been largely applied in the preparation of polysaccharide-based products from renewable sources such as crosslinked starches, and in different applications such as food texturing products (Salay E. and Ciacco C. F., Starch/Staerke, 1990, 42, 15-17; Nabeshima E. H. and Grossmann M. V. E., Carbohydr. Polym., 2001, 45, 347-353; Narkrugsa W. et al., Starch/Staerke, 1992, 44, 81-90; Chang Y.-H and Li C.-Y., J. Food Sci., 1992, 57, 203-205; Kim C.-T. et al., Starch/Staerke, 1999, 51, 280-286).

Glass-like polysaccharide abrasive grits have been prepared by extrusion processes of native or crosslinked starches (US Patent 5,367,068). An extrusion process for the preparation of a crosslinked high amylopectin starch using phosphorous oxychloride as the preferred phosphorous reagent is disclosed in international application WO 97/00620. The products have not been tested for their capacity to absorb water. The products find applications as natural gum replacers.

International application WO 98/35992 discloses the preparation of a crosslinked high amylose starch in batch mode using sodium trimetaphosphate in basic aqueous solution (NaOH), followed by neutralisation with acetic acid, purification by continuous ultrafiltration and spray drying in a Niro™ spray dryer. This multi-step process is rather complex as well as costly as opposed to the extrusion process. The products described in WO 98/35992 are

used as excipients for the controlled release of active ingredients. They have not been disclosed as absorbents or superabsorbents, and their capacity to absorb water was not been compiled.

5       The preparation of crosslinked starch using trisodium  
trimetaphosphate in a co-continuous water-oil system to produce a  
superabsorbent having a maximum absorption of a 0.9 % NaCl solution of 20 g/g  
within one hour, of which 81 % is absorbed within the first five minutes, has been  
described in EP 0900807. In order to remove the oil and to recover the starch-  
phosphate derivative, an organic solvent such as cyclohexane was added,  
10 followed by washing with ethanol. The use of oils and organic solvents, are  
important drawbacks of this batch process when compared to continuous  
extrusion processes.

15       Crosslinked starch granules capable of undergoing  
multiple swelling/drying cycles with very little generation of starch solubles during  
such cycling have been described in WO 99/64508. These starch products can  
be used to good effect in a variety of food products, and have been claimed to  
be part of a thickener composition or a cosmetic or personal care product. A  
batch process was used and the starch was crosslinked using sodium  
trimetaphosphate, sodium tripolyphosphate and mixtures thereof in a NaOH  
20 solution, followed by pH adjustment with hydrochloric acid, centrifugation,  
washes with water and drying at 40 °C. The swelling power of the starch  
derivatives at 25 and 95 °C (SP<sub>25</sub> and SP<sub>95</sub>) was determined by a modification  
of the method disclosed Leach et al. (Leach et al., Cereal. Chem., 1959, 36,  
535).

25       There thus remains a need to develop a more cost  
effective, non abrasive, hypoallergenic, biodegradable, natural and renewable  
polysaccharide-based absorbent, capable of being used alone or in mixtures to  
produce synergistic superabsorbent blends.

30       The present invention seeks to meet these and other  
needs.

The present invention refers to a number of documents, the content of which is herein incorporated by reference.

### **FIELD OF THE INVENTION**

5 The present invention relates to a crosslinked amylopectin obtained by reactive extrusion, possessing high Free Swelling Capacity (FSC) and Improved Centrifuge Retention Capacity (CRC) when compared to unmodified amylopectin or native starches comprising different amylose/amylopectin ratios.

10 The present invention also relates to crosslinked amylopectin to be used as an absorbent or superabsorbent in applications such as personal hygiene products including sanitary napkins and baby diapers, as well as in food pads for the absorption of meat exudates, as well as encapsulating polymers in cosmetic and in pharmaceutical applications (for instance Drug Delivery Systems and Slow Release Substances), as well as for  
15 the delivery of water to the roots of plants, as fire extinguishing devices and in the preparation of artificial snow.

Further scope and applicability will become apparent from the detailed description given hereinafter. It should be understood however, that this detailed description, while indicating preferred embodiments of the invention,  
20 is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

25 Having thus generally described the invention, reference will now be made to the accompanying drawings, showing by way of illustration a preferred embodiment thereof, and in which:

Figure 1 shows the effect of STMP-STPP (99:1) and

NaOH concentrations on the CRC of amylopectin-phosphates.

Figure 2 illustrates the 4 extruding zones, wherein zone 1 is the feed zone; zone 2 is the compression zone; zone 3 is the kneading zone; and zone 4 is the final cooking zone.

## 5 **DETAILED DESCRIPTION OF THE INVENTION**

### **Definitions:**

The term "Free Swell Capacity" (FSC), also called absorption, is expressed in grams (g) of substance absorbed (0.9% NaCl solution) per gram (g) of crosslinked amylopectin.

10 The term "Centrifuge Retention Capacity" (CRC), also called retention, is expressed in grams (g) of substance absorbed (0.9% NaCl solution) per gram (g) of crosslinked amylopectin.

15 The term "Density" refers to the density of the extruded material and is measured after the final product is ground and screened between 30 and 100 mesh. The powder is then weighted in a standardized volumetric cylinder filled with water. The weight obtained (g) is divided by the standard volume ( $\text{cm}^3$ ) of the extrudate. The density is expressed in  $\text{g}/\text{cm}^3$ .

20 The term "Expansion" refers to the expansion of the extruded products and is calculated by measuring the diameter of the extruded product as compared to the die opening. Ten diameter measurements are taken with a micrometer and the mean is divided by the diameter of the die opening, and multiplied by 100.

25 The term "Residence Time" refers to the time taken by the material to get through the extruder, from the feed port to the die. The residence time is measured by adding a small quantity of starch containing a blue edible coloring agent into the feed port. The chronometer is started when the blue starch enters the barrel and is stopped when the extruded product having a blue coloration exits the extruder. The residence time is expressed in seconds.



The term "Screw Pitch" refers to the distance of one pitch of the screw.

The term "Specific Mechanical Energy" (SME) refers to the quantity of energy consumed in KWh by the extruder in order to produce one  
5 kilogram of the extruded material. The specific energy is expressed in KWh/Kg.

The term "Torque" refers to the force exercised by the extruder, expressed in pounds per inch.

The term "Throughput" refers to the amount of extruded material (w) produced over the course of a specific time (t). The "throughput" is  
10 calculated by dividing the weight (w) of extruded material expressed in grams, by the time (t) expressed in seconds. The "throughput" is expressed in grams/second (g/sec).

In a broad sense, the present invention relates to a crosslinked amylopectin having improved Free Swell Capacity (FSC) and  
15 Centrifuge Retention Capacity (CRC). The crosslinking is preferably achieved using phosphorus based reagents such sodium tripolyphosphate, sodium trimetaphosphate, or mixtures thereof. This crosslinked amylopectin offers better performances when compared to native starch and blends of amylose/amylopectin, crosslinked using the same phosphorous reagents.

20 The crosslinked amylopectin of the present invention is prepared by an extrusion process, more specifically reactive extrusion which constitutes an ecological, continuous and economical process. It possesses high free swelling capacity as well as improved centrifuge retention capacity when compared to unmodified amylopectin or native starches containing different  
25 amylose/amylopectin ratios. It is capable of absorbing and retaining water, saline and aqueous solutions, as well as biological fluids such as urine, blood and food exudates. The polysaccharide-based absorbent materials of the present invention can be used as a biodegradable absorbent or superabsorbent in personal hygiene products such as baby diapers, incontinence products, and

sanitary napkins. They can also be used in several other applications such as in food pads; in agricultural and forestry applications to retain water in the soil and to release water to the roots of plants; in fire-fighting techniques; as bandages and surgical pads; for cleaning-up of acidic or basic aqueous solution spills,  
5 including water soluble chemicals spills; as polymeric gels for cosmetics and pharmaceuticals also known as drug delivery systems and slow release substances; and finally for manufacturing artificial snow.

It was previously illustrated in CA 2,308,537 that it is possible to produce a starch-based absorbent by extrusion having very low  
10 absorption performances (reported to be 7.5 g/g in 0.9 % NaCl solution). As disclosed in the detailed description given hereinafter, it was discovered that this process can lead to an absorbent with improved Free Swell Capacity (FSC) and Centrifuge Retention Capacity (CRC) of water, saline and other aqueous solutions and biological fluids. This can be achieved by carefully selecting the  
15 required extrusion parameters such as SME by selecting a specific polysaccharide or starch-based product like amylopectin, and by using a crosslinker such as sodium tripolyphosphate (STPP), sodium trimetaphosphate (STMP) or a mixture of both.

The extend of crosslinking has been reported to be an  
20 important parameter influencing the swelling behavior of a polymer as described in "Modern Superabsorbent Polymer technology" (Buchholz F. L. and Graham A. T. Eds., Wiley-VCH, New York, 1998, pages 170-171). The crosslinkers play an important role in explaining the improvement of the fluids CRC of the crosslinked amylopectin of the present invention.

25 Amylopectin was selected as the preferred polysaccharide due to its very high molecular weight (up to 500 million daltons for potato amylopectin) when compared to the helical structure of amylose (up to 2.65 million daltons). Amylopectin is a highly branched polysaccharide with branches occurring at an average of once every 26 to 40 glucose units through  $\alpha$ -D-(1-6)  
30 linkages (Starch: Chemistry and Technology, Whistler R. L. et al. Eds, second

edition, 1984, Academic Press, New York, p. 255). Furthermore, the branched structure of amylopectin provides for greater solution stability as compared to amylose (Starch: Chemistry and Technology, Whistler R. L. et al. Eds, second edition, 1984, Academic Press, New York, p. 250).

5                    Sodium trimetaphosphate and sodium tripolyphosphate are among the best crosslinking reagents, producing biodegradable phosphate diester linkages. These phosphorous crosslinkers are very well suited to be used in extrusion processes, wherein sodium trimetaphosphate is the preferred phosphorous crosslinking agent. Other crosslinkers can also be used and are  
10 known to those skilled in the art. Examples of other crosslinkers comprise functional epoxides such as diepoxyalkanes, diglycidylether and alkylene bis-glycidyl ethers, dichlorohydrin, dibromohydrin, phosphoryl chloride, phosphoryl oxychlorohydrin, adipic anhydride or other polycarboxylic anhydrides, glyoxal, and glutaraldehyde. A new method for crosslinking starch using polyethylene  
15 glycol dichloride has been recently published (CA 2,362,006). For the preparation of dialdehyde amylopectin, urea and diamines such as hexamethylenediamine and jeffamine<sup>TM</sup> can also be used as crosslinkers.

                  It was discovered that different amylose / amylopectin ratios have a direct impact on the performance of the extruded absorbent  
20 polymer. By keeping the extrusion parameters constant, and by keeping the moisture of the paste constant, it is demonstrated that higher concentrations of amylopectin yields higher performances in terms of the Free Swell Capacity of the absorbent produced. Only pure amylopectin ( $\leq 95\%$  purity) yields a superabsorbent with a Free Swell Capacity higher than 15 g/g with a 0.9 % NaCl  
25 solution as reported in examples 1 to 4.

                  The paste moisture has a direct effect on the Free Swell Capacity (FSC) of the amylopectin extrudate. More specifically, the amount of water used to extrude the amylopectin paste, has a direct impact on the formation of a superabsorbent material. As a matter of fact, a moisture content  
30 ranging between 27 and 32 % is preferred to get a high FSC, as exemplified in

examples 5 to 16. An amylopectin paste having an optimized moisture content ranging from 27 to 32 %, when extruded using specific parameters for factors such as torque, residence time, throughput, and energy, provides an absorbent material.

5                   In the absence of crosslinking, an extrudated absorbent does not have any significant Centrifuge Retention Capacity (CRC) and does not retain a 0.9 % saline solution under pressure (examples 17 to 19). Amylopectin crosslinking can be accomplished by extrusion using a broad range of concentrations of crosslinkers. In order to improve FSC and CRC performances,  
10 a crosslinker composed of 99 % sodium trimetaphosphate and 1 % sodium tripolyphosphate was investigated, in parallel to different concentrations of sodium hydroxide, affecting directly the yield of the crosslinking.

                  It was discovered that concentrations of crosslinkers ranging between 0.001 and 2.0 % (W/W) can be used to get satisfactory FSC  
15 and CRC performances. A preferred crosslinker concentration ranges from about 0.01 to about 0.20 % (W/W), whereas a sodium hydroxide concentration of about 0.02 % (W/W) was found to be optimal (examples 20 to 35).

                  The sodium trimetaphosphate / sodium tripolyphosphate ratio has a direct impact on the FSC and CRC. It is desirable to exclusively use  
20 sodium trimetaphosphate as the sole phosphorus reagent for an optimal CRC (examples 36 to 39).

                  In the present application, a cost effective reactive extrusion process was used to produce an amylopectin-based absorbent. The extrusion parameters, being important factors in the manufacture of an  
25 amylopectin-based absorbent with improved performances in terms of FSC and CRC, were extensively studied. It was found that the temperature of the extruder barrel must be increased gradually from the feeding zone to the die. Furthermore, the temperature of the amylopectin-phosphate extrudate is ranging preferably from about 120 to about 155°C and more preferably from about 130  
30 to about 145°C (examples 40-46).

## **EXPERIMENTAL**

### **Starting Materials:**

Amylopectin, referring to the Powdered Waxy Starch (P.F.P.) 2850, was purchased from Cargill Corporation.

5 Amylose, referring to high amylose starch, was purchased from ADM/Ogilvie.

Sodium Trimetaphosphate (95-97 %), was purchased from Sigma-Aldrich.

10 Sodium Tripolyphosphate (90-95 %), was purchased from Sigma-Aldrich.

Sodium Hydroxide (99 %), was purchased from Laboratoire MAT.

### **TEST METHODS**

As discussed in Modern Superabsorbent Polymer Technology (Buchholz F. L. and Graham A. T. Eds., Wiley-VCH, New York, 1998, section 4.6.1. Swelling Capacity: Theory and Practice, page 147), several methods of measurement are used in order to characterize the swelling capacity of a polymer. In the field of superabsorbents, the Gravimetric Swelling Capacity also called the Free Swell Capacity (FSC)<sup>1</sup>, the Centrifuge Capacity also called 20 the Centrifuge Retention Capacity (CRC)<sup>2</sup>, the Absorption Under Load (AUL) and Swelling Kinetics are recommended methods. In the present invention the FSC and the CRC were used to compare the swelling capacities of the absorbent products obtained.

### **Tea bags for FSC and CRC measurements:**

25 Tea bags (6 x 6 cm) were made from heat sealable Ahlstrom™ filter paper  $16.5 \pm 0.5 \text{ g/m}^2$

**FSC measurements:**

The Free Swell Capacity (FSC) in a 0.9% NaCl solution was determined according to the recommended test method 440.1-99 from EDANA<sup>1</sup>.

**5 CRC measurements:**

The Centrifuge Retention Capacity (CRC) in a 0.9% NaCl solution was determined according to the recommended test method 441.1-99 from EDANA<sup>2</sup>.

**Examples 1 to 4****10 Improvement of the Free Swell Capacity (FSC) using amylopectin.**

Examples 1 to 4 illustrate the effect of the amylose / amylopectin ratio on the Free Swell Capacity of the blends. A Killion KLR 175™ single screw extruder with a L:D ratio of 24:1 was used. The hole opening diameter of the die was 8.44 mm, and the expansion was calculated using this  
15 diameter value.

For each example, a paste was prepared by weighing 5 Kg of the amylose / amylopectin blend (having a moisture content of about 9%), followed by adding 2 Kg of water to get a total moisture content of about 35% (Table 1).

20

**Table 1**

Example	Ratio* (%)	Moisture (%)
1	0.00	33.27
2	38.30	35.30
3	75.10	35.87
4	100.00	35.04

\*Ratio = % amylopectin

The pastes were stabilized over a period of 24 hours and fed into the extruder. The temperatures of the extruder and die were respectively 35, 65, 135, 135, and 135°C for corresponding extruding zones 1,2,3,4 (Figure 2.). The screw speed was kept constant at 50 RPM. The extruded products were dried for 2 days at 60°C and ground in a coffee grinder (Table 2). As can be seen from the results depicted in Table 2, extruded amylopectin, in comparison to extruded mixtures of amylose / amylopectin, gives the best FSC (15.09 g/g).

Table 2

Example	Torque (Lbs-Inch)	Temperature of the extrudate (°C)	Expansion (%)	FSC (g/g)
1	280	124.4	98.10	4.87
2	250	126.7	118.48	6.01
3	330	131.3	115.26	9.52
4	350	131.7	103.55	15.09

10

**Examples 5 to 16****Effect of the amylopectin paste moisture on the Free Swell Capacity (FSC).**

Examples 5 to 16 illustrate the effect of the moisture content on the Free Swell Capacity of the extruded amylopectins. A Davis Standard DS-12HM™ single screw extruder with a L:D ratio of 24:1 was used. The hole opening diameter of the die was 4.82 mm, and the expansion was calculated using this diameter value. For each example, a paste was prepared by weighing 5 Kg of amylopectin (having a moisture content of about 9%) followed by adding different amounts of water to get a moisture content ranging from about 23% to about 32 %. The pastes were stabilized over a period of 24 hours and fed into the extruder. The temperatures of the extruder and die were respectively 50, 75, 135, 135, and 135°C for corresponding extruding zones 1,2,3,4 (Figure 2). The screw speed was kept constant at 25 RPM. The extruded

products were dried for 2 days at 60°C and ground in a coffee grinder (Table 3). As can be seen from the results depicted in Table 3, the best FSC (22.04 and 22.53 g/g) was obtained when the moisture content is between 29 and 31 % (28.91 and 29.29 %).

5

Table 3

Example	Moisture (%)	Temperature of the extrudate (°C)	Expansion (%)	FSC (g/g)
5	23.56	130	135.48	11.07
6	24.97	131	98.13	12.11
7	26.89	131	114.52	10.37
8	27.67	131	166.18	18.16
9	28.37	132	127.80	20.63
10	28.91	132	112.45	22.04
11	29.29	131	124.69	22.53
12	30.18	132	94.19	20.76
13	30.68	132	112.03	21.91
14	30.97	132	108.30	19.69
15	31.24	137	181.12	15.51
16	31.80	136	137.34	14.32

#### Examples 17 to 19

##### **Swelling capacity without crosslinker:**

- Examples 17 to 19 illustrate the reproducibility of the effect of moisture content (%) on the Free Swell Capacity of extruded amylopectins, using different extrusion parameters. A Killion KLR 175™ single screw extruder with a L:D ratio of 24:1 was used. The hole opening diameter of the die was 8.44 mm, and the expansion was calculated using this diameter value. For each example a paste was prepared by weighing 5 Kg of amylopectin (having a moisture content of about 9 %), followed by adding water to obtain a moisture content ranging from about 29% to about 31%. These pastes were stabilized



over a period of 24 hours and fed into the extruder. The temperatures of the extruder and the die were respectively 50, 65, 135, 135, and 135°C for corresponding extruding zones 1,2,3,4 (Figure 2). The screw speed was kept constant at 25 RPM. The extruded products were dried for 2 days at 60°C and ground in a coffee grinder (Table 4). As can be seen from the results depicted in Table 4, the best FSC (22.39 g/g) is obtained when the moisture content is between 29.77 %, and the best CRC (2.90 g/g) is obtained when the moisture content is 31.47 %.

Table 4

Test	Example 17	Example 18	Example 19
Moisture (%)	29.48	29.77	31.47
Pressure (PSI)	270	276	275
Torque (lbs-inch)	260	280	250
Temperature (°C)	132	133	133
Residence Time (sec)	190	140	140
Troughput (g/sec)	1.94	2.34	2.29
Energy (KWh/Kg)	60.05	37.43	38.21
Expansion (%)	87.28	83.97	79.39
FSC (g/g)	20.76	22.39	17.49
CRC (g/g)	1.88	1.84	2.90
Density (g/cm <sup>3</sup> )	0.64	0.67	0.70

**Examples 20 to 35****Effect of STMP:STPP (99:1) and NaOH concentrations on the CRC.**

Examples 20 to 35 illustrate the effect of the crosslinking, using different concentrations of STMP:STPP (99:1) and NaOH, on the Centrifuge Retention Capacity of amylopectin derivatives. A Davis Standard DS-12HM™ single screw extruder with a L:D ratio of 24:1 was used. The hole opening diameter of the die was 4.82 mm, and the expansion was calculated using this diameter value. For each example, a paste was prepared by weighing 5 Kg of amylopectin (having a moisture content of about 9 %) followed by adding an aqueous solution of sodium hydroxide and a mixture of STMP:STPP (99:1) to get a moisture content of about 31 %. The pastes were stabilized over a period of 24 hours and fed into the extruder. The temperatures of the extruder and the die were respectively 50, 75, 135, 135, and 135°C for corresponding extruding zones 1,2,3,4 (Figure 2). The screw speed was kept constant at 50 RPM. The extruded products were dried for 2 days at 60°C and ground in a coffee grinder (Table 5 and Figure 1). As can be seen from the results depicted in Table 5, the best FSC (15.20 g/g) and CRC (14.22 g/g), is obtained using a concentration of STMP:STPP (99:1) of 0.10% (w/w). Furthermore, the best FSC and CRC is obtained using a concentration of sodium hydroxide of 0.2% (w/w).

Table 5

Ex.	STMP:S TPP 99:1 (%W/W)	NaOH (% W/W)	Moisture (%)	Through put (g/sec)	Expansi on. (%)	FSC (g/g)	CRC (g/g)
20	0.00	0.000	31.24	0.94	181.12	15.51	4.08
21	0.00	0.040	31.26	1.20	196.89	12.78	5.96
22	0.00	0.080	31.43	1.09	140.66	14.79	5.32
23	0.10	0.002	30.76	1.19	163.07	14.04	8.38
24	0.10	0.007	30.37	1.18	161.20	14.19	7.57
25	0.10	0.010	30.50	1.28	191.29	14.85	9.61
26	0.10	0.020	31.02	0.88	165.35	15.20	14.22
27	0.10	0.030	30.50	1.37	177.59	12.07	10.85
28	0.10	0.040	31.15	1.19	152.49	10.16	8.25
29	0.10	0.080	31.17	1.00	150.41	7.73	5.91
30	0.50	0.020	31.14	1.09	188.59	13.40	12.30
31	0.50	0.040	31.32	1.10	185.06	8.69	7.61
32	0.50	0.080	30.81	1.03	175.52	7.82	5.37
33	2.00	0.020	30.74	1.15	-	8.51	7.78
34	2.00	0.040	30.81	0.94	-	10.10	9.23
35	2.00	0.080	30.99	1.27	-	6.44	4.96

**Examples 36 to 39****Effect of the STMP:STPP ratio.**

- 5                                      Examples 36 to 39 illustrate the effect of the STMP:STPP ratio on the CRC. A Davis Standard DS-12HM™ single screw extruder with a L:D ratio of 24:1 was used. The hole opening diameter of the die was 4.82 mm, and the expansion was calculated using this diameter value. For each example a paste was prepared by weighing 5 Kg of amylopectin (having a moisture content of about 9%), followed by adding an aqueous solution of 0.020 % NaOH and 0.10 % (W/W) of STMP:STPP in different ratios, to obtain a moisture content of about 32 % (Table 6). The pastes were stabilized over a period of 24 hours and fed into the extruder. The temperatures of the extruder and the die were 35, 65, 135, 135, and 135°C for corresponding extruding zones 1,2,3,4 (Figure 2). The screw speed was kept constant at 25 RPM. The extruded products were then dried for 2 days at 60°C and ground in a coffee grinder (Table 6). The results seem to indicate that the sole presence of STMP is preferred in order to obtain
- 10
- 15

the highest CRC value (14g/g). As can be further observed from Table 6, STMP is the preferred crosslinking agent, reaching an optimal FSC of 14.84 g/g and an optimal CRC of 14.00 g/g.

Table 6

Example	STMP (% W/W)	STPP (% W/W)	Moisture (%)	Extrudat Temp. (°C)	FSC (g/g)	CRC (g/g)
36	100	0	32.23	138	14.84	14.00
37	99	1	32.24	137	13.89	13.35
38	1	99	32.40	138	17.15	10.08
39	0	100	32.56	138	6.57	6.57

5

#### Examples 40 to 46

##### **Effect of the extruder barrel temperatures on performances.**

Examples 40 to 46 illustrate the effect of the temperatures of the extruder barrel on the CRC of amylopectin-phosphates. Amylopectin pastes, with the same concentration of water, STMP and NaOH, were poured in the extruder using the same screw speed. Only the temperatures of the extruder barrel were changed. A Baker Perkins MPF-50D™ extruder, with co-rotative and fully intermeshing twin-screws, was used with a L:D ratio 25. The hole opening diameter of the dies was 6.0 mm and the expansion was calculated using this diameter value. The pastes were prepared by weighing 22.7 Kg of amylopectin (having a moisture content of about 9%) followed by adding 7.58 liters of a 0.02 % aqueous NaOH solution (6.06 g) and 0.10 % (w/w) STMP (30.32 g). The pastes were mixed for 15 minutes in a Leland 100-DA-70™ double action mixer, and fed into the extruder having a moisture content of about 31 %. The temperatures of the extruder barrel were adjusted for every zone of the extruder (zone 1 to 8) as reported in Table 7. The screw speed was kept constant at 50 RPM. The extruded products were dried for 2 days at 60°C and ground in a coffee grinder. The temperature zones of the extruder are compiled in Table 7 and the results are illustrated in Table 8. As can be seen from the results shown in Table 8, the temperature of the extrudate has an effect on the swelling capacity of the

25

products. The optimized extrusion parameters, providing a FSC of 15.04 g/g and a CRC of 13.07 g/g, are shown in Example 45.

Table 7

Example	zone 1 (°F)	zone 2 (°F)	zone 3 (°F)	zone 4 (°F)	zone 5 (°F)	zone 6 (°F)	zone 7 (°F)	zone 8 (°F)
40	90	102	121	150	177	215	273	273
41	104	118	139	160	215	243	287	286
42	121	133	146	185	240	264	296	294
43	119	141	162	193	245	313	301	302
44	118	140	161	192	244	316	312	313
45	118	140	162	205	281	305	323	320
46	89	69	113	132	233	184	188	169

5

Table 8

Example	Pressure (psi)	Extrudat Temp. (°F)	Trough put (g/sec)	FSC (g/g)	CRC (g/g)	Viscosity (cP)
40	100	259	5.26	5.15	4.00	11850
41	70	267	2.99	4.78	4.05	10837
42	100	274	6.78	6.86	5.53	9325
43	120	282	6.92	6.54	5.45	8500
44	80	289	7.25	12.51	11.17	-
45	80	296	5.96	15.04	13.07	5738
46	280	192	-	2.11	0.97	-

Although the present invention has been described hereinabove by way of preferred embodiments thereof, it can be modified without departing from the spirit, scope and nature of the subject invention, as defined in the appended claims.

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## **REFERENCES**

1. EDANA, Free Swell Capacity No. 440.1-99, Recommended test Method: Superabsorbent materials-Polyacrylate superabsorbent powders-Free Swell Capacity in Saline by Gravimetric Determination, Febr. 1999.
- 5 2. EDANA, Centrifuge Retention Capacity No. 441.1-99, Recommended Test Method: Superabsorbent materials-Polyacrylate superabsorbent powders-Centrifuge Retention Capacity in Saline by Gravimetric Determination, Febr. 1999.

**CLAIMS**

1. An absorbent or superabsorbent material comprising a crosslinked amylopectin.
2. An absorbent or superabsorbent material as  
5 defined in claim 1, wherein said amylopectin is crosslinked by a reactive extrusion process.
3. An absorbent or superabsorbent material as defined in claim 1, wherein said absorbent or superabsorbent is produced by crosslinking amylopectin with sodium trimetaphosphate, sodium tripolyphosphate  
10 or a mixture thereof.
4. An absorbent or superabsorbent material as defined in claim 1, wherein said absorbent or superabsorbent is produced by mixing amylopectin, a crosslinker and an alkali solution.
5. An absorbent or superabsorbent material as  
15 defined in claim 1, wherein said amylopectin is a composition of amylose and amylopectin containing at least 95 % amylopectin or its derivatives.
6. An absorbent or superabsorbent material as defined in claim 1, having a centrifuge retention capacity exceeding 5 grams of 0,9 % saline solution per gram of absorbent or superabsorbent material.
- 20 7. An absorbent or superabsorbent material as defined in claim 1, having a free swell capacity exceeding 8 grams of 0,9 % saline solution per gram of absorbent or superabsorbent material.
8. An absorbent or superabsorbent material as defined in claim 1, having a mean particle size comprised between 80 and 800  
25  $\mu\text{m}$ .
9. An absorbent or superabsorbent blend comprising an absorbent or superabsorbent as defined in claim 1 and at least one polymer or copolymer resulting from the polymerization or the graft-polymerization of the

monomers selected from the group consisting of acrylic acid, acrylate alkali salts, acrylic esters, acrylic anhydride, methacrylic acid, methacrylate alkali salts, methacrylic esters, methacrylic anhydride, maleic anhydride, sodium or dissodium maleate, maleate esters, acrylamide, acrylonitrile, vinyl alcohol, vinyl pyrrolidone, vinyl acetate, vinyl guanidine, aspartic acid, and aspartic alkali salts.

10. An absorbent or superabsorbent blend comprising an absorbent or superabsorbent as defined in claim 1 and at least one polymer selected from the mannan polymers and the ionic polymers.

11. An absorbent or superabsorbent blend as defined in claim 11, wherein said mannan polymers are selected from the group consisting of guar gum, tara gum, locust bean gum, Konjac mesquite gum, psyllium extracts and fenugreek extracts.

12. An absorbent or superabsorbent blend as defined in claim 11, wherein said ionic polymers are selected from the group consisting of ionically derivatized polysaccharides, sodium carboxymethyl cellulose, sodium carboxymethyl starch, chitosan, alginate compositions, xanthan gum, carageenan gum, pectin.

13. A blood or menses absorbent member comprising an absorbent or superabsorbent material or formulation as defined in claim 1 or 8 in addition to natural and/or synthetic fibers.

14. A urine, physiological fluids or liquid feces absorbent comprising an absorbent or superabsorbent material or formulation as defined in claim 1 or 8 in addition to natural and/or synthetic fibers.

15. A food fluid exudates absorbent member comprising an absorbent or superabsorbent material or formulation as defined in claim 1 or 8 in addition to natural and/or synthetic fibers.

16. An artificial snow, drug delivery, cosmetic, cat litter absorbent, and soil humidity retaining agent comprising an absorbent or superabsorbent materials or formulations as defined in claim 1 or 8.



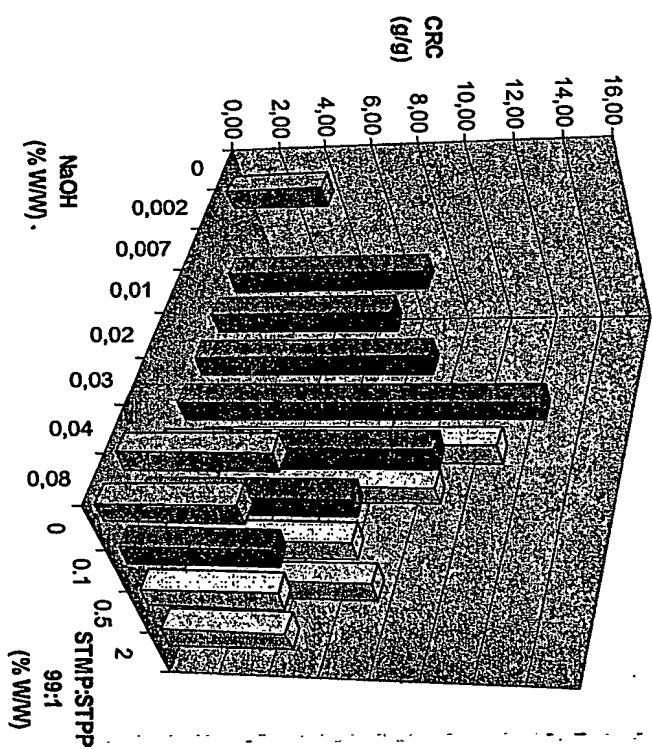


Figure 1.

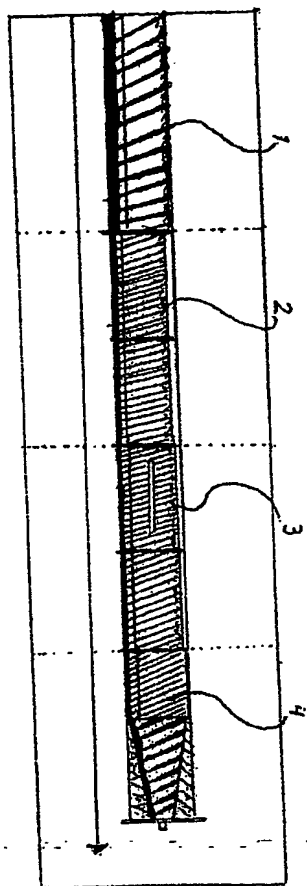


Figure 2.

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